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(54) Title: METHOD FOR THE PRODUCTION OF FILM REAR-INJECTED PLASTIC MOULDED PARTS  
AND FILM REAR-INJECTED PLASTIC MOULDED PARTS

(57) Method for the production of film rear-injected plastic moulded parts comprising a film and a long fiber-reinforced synthetic material, wherein the film is positioned in a moulding tool and rear-injected with a synthetic material reinforced with a fiber material to form a moulded part, wherein the synthetic material and fibre material are added together, melted, and mixed prior to the rear injection in an extruder or an injection moulding machine which have at least one distributive mixing element in the area adjacent to the compression zone, and plastic moulded parts obtained according to this method.



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## Method for the production of film rear-injected plastic moulded parts and film rear-injected plastic moulded parts

### Description

The invention relates to a method for the production of film rear-injected plastic moulded parts, said plastic moulded parts and their use as internal and external body elements, internal airplane components, housings for household appliances and electronics devices, garden furniture, battery cases, window profiles, façade panelling, doors, floor coverings, cell phone housings or seat shells.

Methods to produce reinforced synthetic material films and composite layer films are known to those trained in the art. For example, in EP-A 0 285 071, a multi-layered film comprising a clear layer, a coloured layer and a support layer is described which is rear-injected with an un-reinforced ABS polymer, polybutylene terephthalate, polyamide, polyethylene or polypropylene substrate material. The clear layer used serves as a protective layer for the decorative layer, and is preferred to comprise a mixture of a fluorinated polymer and an acrylic resin. The layering of the composite layer film is done by means of film casting according to the method described. Indeed, this method results in composite moulded parts, but the manufacturing process necessitates drying steps and is technically complicated and thus work- and time-intensive. In addition, the scope of applicability of the moulded parts obtained is necessarily very limited since practicable access to fibre-reinforced composite moulded parts is not indicated.

Similarly complicated is the production of a composite layer film according to EP-A 0 352 298. According to this specification, a composite film is produced first of a coloured layer and a clear layer on a cast film, which is then laminated, coloured layer-side first, onto a substrate film, whereupon the cast film is separated from the clear layer. The individual film layers essentially have the same composition as those described in EP-A 0 285 071. Moreover, in EP-A 0 352 298, a plastic moulding compound is disclosed comprising a filler material, said compound used to strengthen the composite layer film. However, this reinforced plastic moulding compound exhibits an imperfect surface, and thus needs to be coated by the composite layer film mentioned. A further disadvantage is that irregularities in the surface of the reinforced synthetic material can not always be completely avoided or hidden, even with the composite layer film applied thereto.

EP-A 0 442 128 discloses a simplified method to produce multi-layered moulded parts from a deformable film and from thermoplastic or duroplastic resins, wherein this thermally deformable film, which for example can be made of polycarbonate and which can also be printed upon, is placed in a injection moulding tool and moulded via the pressure of the molten rear-injected material and held in position at the same time. Whether multi-layered composite films can also be easily processed into plastic moulded parts according to the method described is not answered, nor is the question of whether it is possible to position the film in the injection moulding tool and to fill this injection moulding tool with fibre-reinforced synthetic materials as well. Moreover, in EP-A 0 442 128, no mention is made as to what condition the film must be in to be used.

According to the German patent application Az 109 28 774.0, rear-injected plastic moulded parts that comprise a multi-layered composite film are produced by co-extruding a multi-layered film made of a cover and a decorative layer, and if necessary with an intermediate layer, in a single process step and directly thereafter rear-injected with a thermoplastic material. However, the moulded part thus obtained, for example comprising a substrate layer of glass-reinforced PBT/ASA, does not always exhibit the proper mechanical behaviour required for all desired applications, mainly with regard to elongation at break and tensile strength. Furthermore, if very long fibre materials are used, a poor visual impression can occur after exposure to temperature changes, which rules out applications in the area of visible components such as exterior body parts. When using glass fibre-reinforced substrate rear-injected compounds, in particular when using long glass fibres, what one also frequently observes is so-called glass nodules on the surface of the moulded parts. These glass nodules have a negative effect both on the visual properties of the moulded parts obtained as well as locally on their mechanical properties. Even if moulded parts are successfully produced that at first have perfect surfaces, unevenness and possibly impairments in shine and colour can not always be avoided in climate change tests, due to these glass nodules.

Therefore, it would be desirable if rear-injected composite film parts were available that do not exhibit the aforementioned disadvantages, and that can be used for a wide variety of applications in the interior and exterior area. It would also be advantageous if the bottom or back of a film rear-injected moulded part had an even appearance that is free of glass nodules or similar visible or detectable glass fibre residues so that these components appear optically perfect in every respect and so that the backs of these components can also be completely acceptable such as for housing or trunk lids.

Thus, the objective of the present invention was to provide a method to produce rear-injected plastic moulded parts in which film rear-injected plastic moulded parts are obtained reproducibly and in a technically simple manner, wherein long fibre-reinforced material is used in the rear-injection of the same and wherein said parts meet the most stringent requirements with regard to mechanical and optical characteristics.

Accordingly, a method to produce film rear-injected plastic moulded parts from a film and from a long fibre-reinforced synthetic material was found in which the film is positioned in a moulding tool and is rear-injected into a moulded part using a synthetic material that is reinforced with a fibre material. In the process, the synthetic material and the fibre material are added to, melted and mixed in an extruder or an injection moulding machine, either of which contains at least one distributive mixing element in the area adjacent to the compression zone, prior to the rear-injection.

Moreover, the film rear-injected plastic moulded parts and their use as internal and external body elements, internal airplane components, housings for household appliances and electronics devices, garden furniture, battery cases, window profiles, façade panelling, doors, floor coverings, cell phone housings or seat shells were found [*sic*].

The construction and composition of the film rear-injected plastic moulded parts according to the invention and their production are described in detail below.

Possible films include single and dual or multi-layered films. Preference is given to dual or multi-layered films, in other words composite layer films. Suitable single-layered films are composed of mixtures of polyamides and polyethylene ionomers, for example, such as ethene/methacrylic acid copolymers containing sodium, zinc and/or lithium counter ions, for example (available under the trade name Surlyn® by

DuPont, among others), or composed of mixtures of copolyesters. However, all other common single-layer films can be used, such as PVC, ABS, ASA, polyester or polycarbonate films. Especially suited are composite-layer films that are made up of at least one substrate layer (1), at least one intermediate or decorative layer (2) if necessary, and at least one transparent cover layer (3), in that order.

The substrate layer (1) contains thermoplastic polymers such as ASA polymers, ABS polymers, polycarbonates, polyesters such as polyethylene terephthalate or polybutylene terephthalate, polyamides, polyether imides, polyether ketones, polyphenylene sulfides, polyphenylene ethers or mixtures of these polymers.

Preferably, ASA polymers are used for the substrate layer. ASA polymers are understood to include impact resistant-modified styrene/acrylonitrile polymers in general in which graft copolymers of vinyl aromatic compounds, in particular styrene, and vinyl cyanides, in particular acrylonitrile, on polyalkyl acrylate rubbers (component A) exist in a copolymer matrix made up of styrene and acrylonitrile (component B) in particular. In another preferred embodiment, preference is given to blends of ASA polymers and polycarbonates. Especially suitable ASA polymers are composed of a graft copolymer (component A) comprising

- a1) 1 to 99 weight-%, preferably 55 to 80 weight-%, in particular 55 to 65 weight-% of a particulate graft base A1 with a glass transition temperature of less than 0°C, preferably less than -20°C, more preferred less than -30°C,
- a2) 1 to 99 weight-%, preferably 20 to 45 weight-%, in particular 35 to 45 weight-% of a graft overlay A2 made of the monomers, based on A2,
  - a21) 40 to 100 weight-%, preferably 65 to 85 weight-% styrene units, substituted styrene units or (meth)acrylic acid ester units, or mixtures thereof, in particular styrene and/or  $\alpha$ -methyl styrene units as component A21 and
  - a22) 0 to 60 weight-%, preferably 15 to 35 weight-% acrylonitrile or methacrylonitrile units, in particular acrylonitrile units as component A22.

Component A1 consists essentially of the monomers

- a11) 80 to 99.99 weight-%, preferably 95 to 99.9 weight-% of at least one C<sub>1</sub>- to C<sub>8</sub> alkyl ester of acrylic acid, preferably n-butyl acrylate and/or 2-ethylhexyl acrylate as component A11,
- a12) 0 to 20 weight-%, preferably 0.01 to 5.0 weight-% of at least one polyfunctional cross-linked monomer, preferably diallyl phthalate and/or dihydrodicyclopentadienyl acrylate (DCPA) as component A12.

The acrylate rubbers A1 are preferred to be alkyl acrylate rubbers comprising one or more C<sub>1</sub>- to C<sub>8</sub>-alkyl acrylates, preferably C<sub>4</sub>- to C<sub>8</sub>-alkyl acrylates, wherein preferred use is made of at least some butyl-, hexyl-, octyl- and/or 2-ethylhexyl acrylate, in particular n-butyl and/or 2-ethylhexyl acrylate.

These acrylate rubbers A1 preferably contain 0.01 to 20 weight-%, preferably 0.1 to 5 weight-% cross-linking bi-functional or polyfunctional monomers (cross-linking monomers), based on the total amount of A1. Examples of this are monomers that contain two or more double bonds capable of copolymerization and that are preferably not conjugated in the 1,3 position. Suitable cross-linking monomers include divinyl benzene, diallyl maleate, diallyl fumarate, diallyl phthalate, triallyl cyanurate, triallyl isocyanurate, tricyclodeceny acrylate, dihydrodicyclopentadienyl acrylate, triallyl phosphate, allyl acrylate, allyl methacrylate, for example. An especially favourable cross-linking monomer has proven to be dihydrodicyclopentadienyl acrylate (DCPA: see DE-C 12 60 135). Up to 30 weight-% of monomers that form "hard" polymers, such as vinyl acetate, (meth)acrylonitrile, styrene, substituted styrene, methyl methacrylate and/or vinyl ether, based on the total weight of A1, can be polymerized into the alkyl acrylate rubber A1.

According to an embodiment of the invention, possible graft bases A1 include cross-linked acrylic acid ester polymers with a glass transition temperature of below 0°C. The cross-linked acrylic acid ester polymers should have a preferred glass transition temperature of below -20°C, in particular below -30°C.

According to a preferred embodiment, the graft base A1 is composed of 15 to 99.9, in particular 70 to 99.0 weight-% of C<sub>1</sub>- to C<sub>8</sub>-alkyl esters of acrylic acid, 0.1 to 5, in particular 0.1 to 3 weight-% of cross-linking agents and 0 to 49.9, in particular 0 to 20

weight-% of one of the other monomers or rubbers indicated.

Examples of suitable monomers to form graft overlay A2 in the form of component A21 include styrene, substituted styrenes such as singly or multiply substituted alkyl and/or halogen styrenes, for example  $\alpha$ -methyl styrene, and (meth)acrylic acid esters such as methyl methacrylate, 2-ethylhexyl acrylate and n-butyl acrylate, in particular methyl methacrylate. Suitable as component A22 are acrylonitrile and methacrylonitrile, in particular acrylonitrile.

Component A is preferred to be a graft copolymer. Graft copolymers A generally have an average particle size  $d_{50}$  of 50 to 1000 nm, preferably 50 to 800 nm and more preferably from 50 to 600 nm. Preferred particle sizes of the graft base A1 are in the range of 50 to 350 nm, preferably from 50 to 300 nm and more preferably from 50 to 250 nm.

The graft copolymer A can be constructed in one or more stages, in other words the graft core is enveloped by one or more graft shells. Numerous graft shells are in general applied by grafting onto the rubber particles in steps, whereby each graft shell can have a different composition. In addition to the grafting monomers, monomers containing polyfunctional cross-linking or reactive groups can be co-grafted (see also EP-A 230 282, DE-AS 36 01 419 and EP-A 269 861).

In a preferred embodiment, component A consists of a multi stage-constructed graft copolymer, wherein the graft stages are in general made of resin-forming monomers and exhibit a glass [transition] temperature  $T_g$  above 30°C, preferably above 50°C. The multi-stage construction contributes to a (partial) compatibility of the rubber particles A with component B, among other things.

According to another preferred embodiment of the invention, the particle size distribution of component A is bimodal, wherein in general 60 to 90 weight-% have a mean particle size of 50 to 200 nm and 10 to 40 weight-% have a mean particle size of 50 to 400 nm, based on the total weight of component A.

The mean particle size and particle size distribution provided are the parameters determined from integral mass distribution. The mean particle size according to the

invention is always the weight-average of the particle sizes as determined using an analytic ultracentrifuge in accordance with the method of W. Scholtan and H. Lange, *Kolloid-Z. und Z.-Polymere* 250 (1972), pages 782-796. The ultracentrifuge measurement provides the integral mass distribution of the particle diameter of a sample. From this, one can deduce the weight percentage of particles that have a diameter that is equal to or smaller than a specific amount. The average particle diameter, which is also identified by the  $d_{50}$  value of the integral mass distribution, is defined as the particle diameter at which 50 weight-% of the particles have a smaller diameter than the diameter to which the  $d_{50}$  value corresponds. Likewise, then, 50 weight-% of the particles have a larger diameter than the  $d_{50}$  value. To characterize the width of the particle size distribution of the rubber particles, the  $d_{10}$  and  $d_{90}$  values derived from the integral mass distribution are used, in addition to the  $d_{50}$  value (average particle diameter). The  $d_{10}$  and  $d_{90}$  value of the integral mass distribution is defined in the same way as the  $d_{50}$  value, with the difference being that they are relative to 10 and 90 weight-% of the particles, respectively. The quotient  $(d_{90}-d_{10})/d_{50}$  represents a measure of the distribution width of the particle sizes. The smaller the Q value, the narrower the distribution.

Graft copolymers A can be produced through emulsion, solution, bulk or suspension polymerization. Preferably, radical emulsion polymerization is used wherein monomers A21 and A22 are grafted in the presence of lattices of component A1 at temperatures of up to 90°C using water-soluble or oil-soluble initiators such as peroxodisulfate or benzyl peroxide, or using redox initiators. Redox initiators can also be used for polymerizations below 20°C.

Suitable emulsion polymerization methods are described in DE-A 28 26 925, DE-A 31 49 358 and in DE-C 12 60 135, for example.

Graft shell construction through emulsion polymerization is also described in DE-A 32 37 555, DE-A 31 49 357, DE-A 31 49 358 and DE-A 34 14 118. The particle size of component A can be adjusted, preferably according to the methods disclosed in DE-C 12 60 135, DE-A 28 26 925 and in Applied Polymer Science, Volume 9 (1965), page 2929, also in particular to values in the range of 50 to 1000 nm. Polymers with different particle size distributions are producible according to DE-A 28 26 925 and US-A 5 196 480, for example.



For example, according to the method described in DE 12 60 135, the graft base A1 can be produced first by polymerizing C<sub>1</sub>- to C<sub>8</sub>-alkyl esters of acrylic acid and cross-linking monomers, if necessary together with other co-monomers, in an aqueous emulsion in a known manner at temperatures of between 20 and 100°C, preferably between 50 and 80°C. Common emulsifiers such as alkali salts of alkyl or alkylaryl sulfonic acids, alkyl sulfates, fatty alcohol sulfonates, salts of higher fatty acids with 10 to 30 carbon atoms or rosins can be used. Preferably, sodium salts of alkyl sulfonates or fatty acids with 10 to 18 carbon atoms are used. According to one embodiment, the emulsifiers are added in amounts of 0.5 to 5 weight-%, in particular 1 to 2 weight-%, based on the monomers used in the production of the graft base A1. In general, a weight-ratio of water to monomer of 2 : 1 to 0.7 : 1 is used. Possible polymerization initiators include in particular the usual persulfates such as potassium persulfate. However, redox systems can also be put to use. The initiators are in general added in amounts of 0.1 to 1 weight-%, based on the monomers used in the production of the graft base A1. Other polymerization aids can include common buffer substances such as sodium bicarbonate or sodium pyrophosphate, by means of which the pH is adjusted to preferably 6 to 9, as well as 0 to 3 weight-% of a molecular weight regulator such as mercaptans, terpinols or dimeric  $\alpha$ -methyl styrene.

According to an embodiment of the invention, the latex obtained from the cross-linked acrylic acid ester polymer is grafted with a monomer mixture of a vinyl aromatic compound (component A21), for example styrene, and a vinyl cyanide (component A22), for example acrylonitrile. The weight ratio of, for example, styrene to acrylonitrile in the monomer mixture is in the range of 100:0 to 40:60, preferably in the range of 63:35 to 85:15. Advantageously, this graft copolymerization is again carried out in aqueous emulsion under the usual conditions described above. It is useful for the graft copolymerization to proceed in the same system as the emulsion polymerization to produce the graft base A1, wherein another emulsifier and/or initiator is added if necessary. The monomer mixture of styrene and acrylonitrile can be added to the reaction mixture all at once, batch-wise in multiple steps or preferably continuously during the polymerization. The graft copolymerization of this mixture in the presence of cross-linked acrylic acid ester polymer is preferably carried out so that a degree of grafting in the graft copolymer A of 1 to 99 weight-%, preferably 20

to 45 weight-%, in particular 35 to 45 weight-%, results, said percentage being based on the total weight of component A. Since the graft yield usually does not reach 100% in graft copolymerization, a somewhat larger amount of monomer mixture of styrene and acrylonitrile is frequently used than would correspond to the desired degree of grafting. Controlling the graft yield during graft copolymerization and thus of the degree of grafting of the finished graft copolymer A is a process with which one trained in the art is accustomed and can occur by controlling the dosing rate of the monomers or by adding a polymerization regulator, among other things (Chauvel, Daniel, ACS Polymer Preprints 15 (1974), page 329 ff.). In general, about 5 to 15 weight-% based on graft copolymer A remains as free, un-grafted styrene/acrylonitrile copolymer in emulsion graft copolymerization. The fraction of graft copolymer A in the polymerization product obtained through graft copolymerization is determined according to the method indicated above.

In the production of graft copolymers A according to the emulsion method, reproducible particle size modifications are also possible in addition to the processing advantages indicated. This includes particle size enlargement through at least partial agglomeration of the particles. This means that in graft copolymers A, polymers can also exist that have different particle sizes.

Component B is a copolymer that contains essentially

- b1) 40 to 100 weight-%, preferably 60 to 85 weight-% of units of styrene, substituted styrene or of a (meth)acrylic acid ester or mixtures thereof, in particular units of styrene and/or  $\alpha$ -methyl styrene as component B1, and
- b2) 0 to 60 weight-%, preferably 15 to 40 weight-% of units of acrylonitrile or methacrylonitrile, in particular acrylonitrile as component B2.

According to a preferred embodiment of the invention, the viscosity index of component B is 50 to 90, preferably 60 to 80, determined according to DIN 53 726 in a 0.5 weight-% solution in dimethyl formamide.

Preferably, component B is an amorphous polymer, for example as is described above as graft overlay A2. According to an embodiment of the invention, a copolymer of styrene and/or  $\alpha$ -methyl styrene with acrylonitrile is used as component B. The

acrylonitrile content in these copolymers of component B is in general 0 to 60 weight-%, preferably 15 to 40 weight-% based on the total weight of component B. The free, un-grafted copolymers of vinyl aromatic compounds and vinyl cyanides, such as styrene/acrylonitrile copolymers that arise during graft copolymerization in the production of component A also count as component B. Depending on the conditions selected for the graft copolymerization for the production of graft copolymer A, it can be possible that during the graft copolymerization a sufficient fraction of component B has already been formed. In general, however, it is necessary to admix the products obtained during the graft copolymerization with additional, separately produced component B. Components A1 and B need not have the same composition of course.

This additional, separately produced component B is preferred to be a styrene/acrylonitrile copolymer, an  $\alpha$ -methyl styrene/ acrylonitrile copolymer or an  $\alpha$ -methyl styrene/ styrene/ acrylonitrile terpolymer. These copolymers can be used individually or as a mixture for component B such that the additional, separately produced component B can be a mixture of a styrene/acrylonitrile copolymer and an  $\alpha$ -methyl styrene/ acrylonitrile copolymer, for example. In the case where component B consists of a mixture of a styrene/acrylonitrile copolymer and an  $\alpha$ -methyl styrene/acrylonitrile copolymer, the acrylonitrile content of the two copolymers should preferably not deviate by more than 5 weight-% from one another, based on the total weight of the copolymer. Component B can, however also consists just of a single copolymer of vinyl aromatic compounds and vinyl cyanides if in the graft copolymerization to produce component A and in the production of the additional, separately produced component B the same monomer mixture is used as the starting material.

The additional, separately produced component B can be obtained through conventional methods. Thus, according to an embodiment of the invention, the copolymerization of styrene and/or  $\alpha$ -methyl styrene with acrylonitrile, for example, can be carried out in bulk, solution, suspension or aqueous emulsion.

In a preferred embodiment, the substrate layer (1) contains polycarbonates and if necessary other additives as described below as an additional component in addition to components A and B.

Suitable polycarbonates are well known. As pertains to the invention, polycarbonates meant here include copolycarbonates as well. Polycarbonates are preferred to have a molecular weight (weight-average  $M_w$ , determined through gel permeation chromatography in tetrahydrofuran against a polystyrene standard) in the range of 10000 to 200000 g/mol. Preferably, it is in the range of 15000 to 100000 g/mol. This means that the polycarbonates in general have relative solution viscosities in the range of 1.1 to 1.5, measured in a 0.5 weight-% solution in dichloromethane at 25°C, preferably from 1.15 to 1.33.

Polycarbonates are obtained via interface polycondensation according to the method of DE-B-1 300 266, for example, or via the reaction of diphenyl carbonate with bisphenols according to the method of DE-A-1 495 730. Preferred bisphenol is 2,2-Di(4-hydroxyphenyl)propane, generally identified as bisphenol A – as is used below as well. Commercially available polycarbonates include Makrolon® (by Bayer) and Lexan® (by GE Plastics), for example.

Instead of Bisphenol A, other aromatic dihydroxy compounds can also be used, in particular 2,2-di(4-hydroxyphenyl) pentane, 2,6-dihydroxynaphthalene, 4,4'-dihydroxydiphenyl sulfone, 4,4'-dihydroxydiphenyl ether, 4,4'-dihydroxydiphenyl sulfite, 4,4'-dihydroxydiphenyl methane, 1,1-di-(4-hydroxyphenyl) ethane, 4,4'-dihydroxydiphenyl or dihydroxydiphenylcyclo alkanes, preferably dihydroxydiphenylcyclo hexanes or dihydroxycyclo pentanes, in particular 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane as well as mixtures of the above dihydroxy compounds.

Especially preferred polycarbonates are those based on resorcinol or resorcinol arylates and based on bisphenol A or bisphenol A together with up to 80 mol-% of the aromatic dihydroxy compounds mentioned above. Copolycarbonates according to US 3,737,409 can also be used. Of particular interest are copolycarbonates based on bisphenol A and bis-(3,5-dimethyl-4-hydroxyphenyl) sulfone or 1,1-di-(4-hydroxyphenyl)-3,3,5-trimethyl-cyclohexyl, which are characterized by a high thermal shape stability. The latter copolycarbonate is also commercially available

under the trade name Apec®HT (by Bayer). It is further possible to use mixtures of different polycarbonates.

The polycarbonates can be used both as ground material and in granulated form. They usually exist in the ASA substrate layer in amounts of 0 to 50 weight-%, preferably from 10 to 40 weight-%, based on the total moulding compound respectively.

The addition of polycarbonates leads to higher thermal stability among other things, and to improved crack resistance of the compound films.

Mixing components A, B and if necessary the polycarbonates can be done according to any arbitrary manner according to all known methods. If components A and B for example, had been produced via emulsion polymerization, it is possible to mix together the polymer dispersions obtained, whereupon the polymers are precipitated together and the polymer mixture is prepared. Preferably, however, the admixing of components A and B is done through co-extrusion, kneading or rolling of the components, preferably at temperatures in the range of 180 to 400°C, wherein the components had been isolated from solution or from the aqueous dispersion obtained during the polymerization beforehand, if necessary. The graft copolymerization products (component A) obtained in aqueous dispersion can also be only partially de-watered and mixed with component B as moist crumbs, wherein the complete drying of the graft copolymers is then carried out during mixing.

It can be advantageous to pre-mix individual components. Also, the mixing of components in solution and removal of the solvent is possible. Preferred organic solvents include chlorobenzene, mixtures of chlorobenzene and methylene chloride or mixtures of chlorobenzene or aromatic hydrocarbons, such as toluene. The evaporation of solvent mixtures can be done in evaporating extruders, for example. The components can be dosed together or separately/in succession.

The substrate layer (1) made of component A, B and if necessary polycarbonates, can furthermore contain additive compounds that are typical and common for the (co)polymers described, i.e. polycarbonates, SAN polymers or graft copolymers as well as mixtures thereof. Additives can include: dyes, pigments, colour enhancers,

antistatic agents, antioxidants, stabilizers for improved thermal stability, to increase light stability, to increase hydrolysis resistance and chemical resistance, means to prevent thermal decomposition and in particular lubricants/slip agents that are helpful in the production of moulded parts. The dosing of these further additives can be done at any stage of the production process, but preferably at an early stage in order to utilize the stabilizing effect (or other special effect) of the additive early on. Thermal stabilizers or oxidation retardants are usually metal halogenides (chlorides, bromides, iodides) that derive from Group I metals in the periodic system of the elements (such as Li, Na, K).

Suitable stabilizers include the common hindered phenols, such as 2,6-disubstituted phenols like bis(2,6-tert-butyl)-4-methyl phenol (BHT), 4-methoxymethyl-2,6-di-tert-butyl phenol, 2,6-di-tert-butyl-4-hydroxymethyl phenol, 2,2-bis-(4-hydroxyphenyl) propane, 4,4'-dihydroxybiphenyl and bis(2,6-methyl)-4-methyl phenol; wherein bis(2,6-(C<sub>1</sub>- to C<sub>10</sub>-alkyl)-4-(C<sub>1</sub>- to C<sub>10</sub>-alkyl) phenols are preferred. Other options include vitamin E, or similarly constructed compounds. Moreover, so-called HALS stabilizers (Hindered Amine Light Stabilizers) are also suitable, including tetraalkyl piperidine-N-oxy compounds, benzophenones, resorcins, salicylates and benzotriazoles such as Tinuvin®P (2-(2H-benzotriazole-2-yl)-4-methyl phenol). These are usually used in amounts of up to 2 weight-% based on the entire mixture.

Suitable lubricants and de-moulding agents include stearic acids, stearyl alcohol, stearic acid esters or general higher fatty acids, derivatives and corresponding fatty acid mixtures thereof with 12 to 30 carbon atoms. The amounts of these additives are in the range of 0.05 to 1 weight-% based on the entire mixture.

Silicone oils, oligomeric isobutylene or similar materials are possible additives, and are usually present in amounts of 0.05 to 5 weight-% based on the entire mixture. Pigments, dyes, optical brighteners, colour enhancers, such as titanium dioxide, carbon black, iron oxides, phthalocyanines, chinacridones, perylenes, anthrachinones, aluminium glitter can also be used.

Processing aids, such as lubricants and stabilizers like UV stabilizers, as well as antistatic agents are commonly used together in amount of 0.01 to 5 weight-%.

Instead of ASA polymers or blends thereof with polycarbonates, or in addition to these, the substrate layer (1) can also contain ABS polymers (these include, among other things impact resistant-modified styrene/acrylonitrile polymers in which graft copolymers of styrene and acrylonitrile on polybutadiene rubbers exist in a copolymer matrix of styrene and acrylonitrile), polycarbonates, polyesters such as polybutylene terephthalate (PBT) or polyethylene terephthalate (PET), polyamides, polyether imides (PEI), polyether ketones (PEK), polyphenylene sulfides (PPS), polyphenylene ethers or blends of these polymers. The above polymer materials are known in general, for example from H. Domininghaus, *Die Kunststoffe und ihre Eigenschaften*, VDI Verlag, Düsseldorf (1992).

In a preferred embodiment, the substrate layer (1) is made up of ASA polymers, mixtures of ASA polymers and polycarbonates, ABS polymers, polycarbonates, polybutylene terephthalate, polyethylene terephthalate, polyamides or blends of ASA polymers and polybutylene terephthalate. It is especially preferred that the substrate layer (1) contain a moulding compound comprising ASA polymers or mixtures of ASA polymers and polycarbonates. They can also consist essentially or completely of these polymers.

The layer thickness of the substrate layer (1) is preferred to be 100 to 2000  $\mu\text{m}$ , in particular 150 to 1500  $\mu\text{m}$  and more preferably 200 to 1000  $\mu\text{m}$ .

In another embodiment, the composite layer films have an intermediate layer (2) made of thermoplastic and/or duroplastic synthetics, if necessary with other additives. Suitable thermoplastic synthetics include the polyalkyl and/or aryl esters of (meth)acrylic acid, poly(meth)acrylamides or poly(meth)acrylonitrile, also known as acrylic resins, as well as ABS polymers, styrene/acrylonitrile polymers (SAN), polycarbonates, polyesters, such as polyethylene or polybutylene terephthalate, polyamides, in particular amorphous polyamide, for example polyamide 12, polyether sulfones, thermoplastic polyurethanes, polysulfones, polyvinyl chloride or ASA polymers. Also, blends of the above (co)polymers are basically suitable, such as mixtures of ASA polymers and polycarbonates as described above for the substrate layer (1). Also, thermoplastic polyurethanes, in particular weather-resistant aliphatic polyurethanes, such as commercial product Elastollan® (by Elastogran, Lemförde) (see also *Kunststoff-Handbuch, Polyurethane*, Volume 7, 2<sup>nd</sup> Edition, Carl Hanser

Verlag, Munich, 1983, pages 31 to 39), are possible film materials. Preference is given to acrylic resins, polycarbonates and/or styrene (co)polymer.

Suitable acrylic resins include poly(meth)acrylates, i.e. esters of acrylic and methacrylic acid and mixtures of these polymers or copolymers of acrylates and methacrylates. Preference is given to polyalkyl methacrylates, as well as those in impact resistant modified form, in particular to polymethyl methacrylate (PMMA) or impact resistant-modified polymethyl methacrylate (HI-PMMA). In a preferred embodiment, PMMA contains a fraction of (meth)acrylate comonomers such as n-butyl (meth)acrylate or methyl acrylate, which is in general not more than 20 weight-%. Impact resistant PMMA (High Impact PMMA: HI-PMMA) is a polymethyl methacrylate that is made impact resistant via suitable additives. Impact resistant modifiers can include EPDM rubbers, polybutyl acrylate, polybutadiene, polysiloxanes or methacrylate/butadiene/styrene (MBS) and methacrylate/acrylonitrile/butadiene/styrene copolymers. Suitable impact resistant modified poly(meth)acrylates are described in M. Stickler, T. Rhein in Ullman's encyclopedia of industrial chemistry, Vol. A21, pages 473-486, VCH Publishers Weinheim, 1992, and H. Domininghaus, *Die Kunststoffe und ihre Eigenschaften*, VCI Verlag Düsseldorf, 1992. Suitable polymethyl methacrylates are otherwise known to one trained in the art and for example available under the trade names Lucryl® (BASF AG) and Plexiglas® (Röhm GmbH).

Polyesters meant here include the higher to high molecular esterification products of doubly valent acids, in particular terephthalic acid, with doubly valent alcohols, primarily ethylene glycol. Of the polyalkylene terephthalates, polyethylene terephthalate (PET) is especially suitable. PET commercial products include Arnite® (by Akzo), Grilpet® (by EMS-Chemie) and Valox® (by GE Plastics), for example.

Finally, thermoplastic polyurethanes (TPU) are the reaction products of diisocyanates with long-chained diols. In contrast to polyurethane foams made of polyisocyanates (containing at least three isocyanate groups) and multivalent alcohols (containing at least three hydroxy groups), in particular polyether and polyester polyols, thermoplastic polyurethanes have no or only minimal cross-linking and accordingly have a linear structure. Thermoplastic polyurethanes are sufficiently known to one trained in the art and are described in *Kunststoff Handbuch*, Volume 7, Polyurethanes, published by G. Oertel, 2<sup>nd</sup> Edition, Carl Hanser Verlag, Munich, 1983, in particular



on pages 428 to 473, for example. An example of a commercially available product is Elastolan® (by Elastogran GmbH).

Suitable duroplastic synthetics include polyurethane foams, for example, such as so-called polyester foams and in particular polyether foams. This class of compounds is sufficiently known to one trained in the art and is described in *Kunststoff Handbuch*, Volume 7, Polyurethane, published by G. Oertel, 2<sup>nd</sup> Edition, Carl Hanser Verlag, Munich, 1983, in particular on pages 170 to 246, among other places.

Preference is given to acrylic resins and/or styrene (co)polymers.

The intermediate layer (2) can act as a colouring layer or decorative layer. It is preferred to be constructed of impact resistant polymethyl methacrylates (PMMA), polycarbonates or the ASA polymers described above for the substrate layer (1), or blends thereof with polycarbonates. The intermediate layer (2) can also contain colour enhancers. This includes for example dyes, metal flakes or pigments. Possible dyes or pigments include organic or inorganic compounds. Possible organic pigments include coloured, white and black pigments (colouring pigments) as well as liquid crystal pigments. Suitable inorganic pigments also include colouring pigments and shine pigments and the inorganic pigments commonly used as fillers. Of course, different organic, inorganic or even combinations of organic and inorganic pigments can be used.

In another embodiment, the substrate layer (1) contains the previously mentioned colour enhancers – alone or together with an intermediate layer (2), if necessary.

The layer thickness of the decorative layer (2) is in general in the range of 10 to 1000, preferably 50 to 500 and more preferably from 100 to 400 µm.

For the cover layer (3) of the composite layer film, preference is generally given to poly(meth)acrylate polymers. Particularly suitable are polymethyl methacrylates (PMMA) as a cover layer material, for example as described in EP-A 0 255 500. PMMA with average molecular weights in the range of 40,000 to 100,000 g/mol is referred. Suitable PMMA moulding compounds include products that are available under the trademark Lucryl® (BASF AG), for example.

The cover layer (3) is in general translucent, preferably transparent. Instead of poly(meth)acrylate polymers or together with them, impact resistant poly(meth)acrylates, in particular impact resistant polymethyl methacrylate, fluorine (co)polymers such as polyvinylidene fluoride (PVDF), ABS polymers, polycarbonates, polyethylene terephthalate, amorphous polyamide, polyether sulfones, polysulfones or SAN copolymers can also be used. In particular, the cover layer contains polymethyl methacrylate, impact resistant polymethyl methacrylate or polycarbonates, preferably polymethyl methacrylate, impact resistant polymethyl methacrylate, PVDF or mixtures thereof. The polymers or mixtures thereof are generally selected such that they result in a transparent cover layer.

Suitable fluorine (co)polymers are formed from olefinically unsaturated monomers or comonomers, in which at least one  $sp^2$  carbon is bonded to at least one fluorine atom covalently. These (co)monomers include chlorotrifluoroethene, fluorovinylsulfonic acid, hexafluoroisobutene, hexafluoropropene, perfluorovinylmethyl ether, tetrafluoroethene, vinyl fluoride and in particular vinylidene fluoride. The weight-averaged molecular weight of fluorine (co)polymers is usually in the range of 50,000 to 300,000, preferably in the range of 100,000 to 200,000 g/mol. Mixtures of fluorine (co)polymers and poly(meth)acrylates can also be used. Mixtures of polyvinylidene fluoride (PVDF) and polymethyl methacrylate are preferable. The fraction of PVDF is advantageously in the range of 40 to 80, preferably 55 to 75 weight-% in these mixtures, based on the total weight of the mixture.

In another embodiment, the cover layer is derived from a radiation-cured compound that contains ionically and in particular radically curable functional groups. The radical radiation-cured cover layer is preferred to contain i) polymers with ethylenically unsaturated groups or ii) mixtures of these polymers with ethylenically unsaturated low molecular weight compounds or iii) mixtures of thermoplastic polymers without ethylenically unsaturated groups with ethylenically unsaturated compounds.

Possible ethylenically unsaturated groups in the polymer i) can be maleic acid, fumaric acid, maleic acid anhydride or (meth)acrylic acid radicals. Suitable polymers i) can be based on polyester, polyethers, polycarbonates, polyepoxides or polyurethanes.

Possible ethylenically unsaturated low-molecular weight compounds include alkyl (meth)acrylates such as methyl methacrylate, methyl acrylate, n-butyl acrylate, ethyl acrylate [*sic*], or 2-ethylhexyl acrylate, vinyl aromatics such as vinyl toluene or styrene, vinyl esters such as vinyl stearate or vinyl acetate, vinyl ethers such as vinyl methyl ether, acrylonitrile or methacrylonitrile, for example.

Suitable saturated thermoplastic polymers include polymethyl methacrylate, impact resistant polymethyl methacrylate, polystyrene, impact resistant polystyrene (HIPS), polycarbonate or polyurethanes, for example.

The radiation-cured compound can contain photo-initiators, flow agents or stabilizers as additional components, such as UV absorbers and radical capturing agents.

The radiation curing of the cover layer proceeds using high-energy radiation, such as UV light or electron radiation, if necessary at increased temperatures.

For further details with regard to the composition of the radiation-cured cover layer and its manufacture, expressed reference is made here to WO 99/63015.

Moreover, an adhesive layer made of an adhesion promoter with a layer thickness of in general 5 to 400, in particular 5 to 100  $\mu\text{m}$  can be placed on the outer surface of the substrate layer. The purpose of the adhesion promoters is to produce a solid connection to a selected substrate that lies beneath the substrate layer (for example by rear-injection). The adhesive layer is then used if the adhesion of this further substrate to the substrate layer is insufficient (for example for polyolefin substrates). Suitable adhesion promoters are known to one trained in the art. Examples of suitable adhesion promoters are ethylene-vinyl acetate copolymers to couple to polyethylene and maleic acid anhydride grafted polypropylenes to couple to polypropylene. In both cases, the current opinion is that adhesion is accomplished by polar groups being introduced to non-polar polyolefins.

Rear-injected or composite layer films comprising a substrate layer (1), if necessary an intermediate or decorative layer (2), a cover layer (3) and if necessary an adhesive layer (0) usually exhibit the following layer thicknesses;

Substrate layer (1): 100 to 2000  $\mu\text{m}$ , preferably 150 to 1500  $\mu\text{m}$  and more preferably 200 to 1000  $\mu\text{m}$ ,

Intermediate layer (2): : 0 to 1000  $\mu\text{m}$ , preferably 50 to 500  $\mu\text{m}$ , more preferably 70 to 400  $\mu\text{m}$ , and in particular 100 to 300  $\mu\text{m}$ ,

Cover layer (3): 20 to 300  $\mu\text{m}$ , preferably 50 to 200  $\mu\text{m}$ , and more preferably 50 to 100  $\mu\text{m}$  and

Adhesive layer (0): 0 to 400  $\mu\text{m}$ , preferably 10 to 200  $\mu\text{m}$  and more preferably 50 to 100  $\mu\text{m}$ .

The overall thickness of this composite layer film is usually in the range of 150 to 2000  $\mu\text{m}$ , preferably 250 to 1500  $\mu\text{m}$  and more preferably 200 to 1000  $\mu\text{m}$ .

For example, starting with a composite layer film of the two layers (2) and (3), a three-layer film can be produced by subsequently providing the aforementioned layer with a substrate layer (1). To produce the composite layer film, it is in general advantageous if the magnitude ratio of the MFI value (melt flow index) of the individual components of the composite layer film be a maximum of 3:1, and especially preferred a maximum of 2:1. This will allow the maximum MFI value of any of the components (0), (1), (2), (3) if they exist in the respective composite layer films, to be no more than three times, and especially preferred no more than two times the lowest MFI value. This will ensure an even flow behaviour of all components used in the composite layer plates or films. This mutually tailored flow behaviour is advantageous in particular if the composite layer films are produced through adapter- or nozzle co-extrusion of the components. Here, it is preferable for the entire composite to be produced in a single stage process. In particular, in the adapter co-extrusion process, it is advantageous to tailor the flow characteristics of the individual components to construct even layers.

Nozzle co-extrusion, in particular utilizing "membrane nozzle technology", has the advantage of enabling, for example, a higher orientation of metal glitter and thus a better appearance of a metallic paint coating. The individual components are made to flow easily in extruders and brought into contact with one another via special equipment such that composite films result with the above described sequence of

layers. For example, the components can be co-extruded through a wide slit nozzle. This method is explained in EP-A2-0 225 500 for example.

The production of composite layer films according to the adapter co-extrusion process is described in the extrusion technology convention publication "*Coextusion von Folien*", 8/9 October 1996, VDI Verlag Düsseldorf, in particular in the paper by Dr. Netze. This economical process is used in most co-extrusion applications.

Furthermore, the composite layer films can be produced by laminating the individual film layers one on top of the other in a heatable gap. In the process, films of the individual components are first produced. This can be done according to known methods. Then, the desired layer sequence is produced by placing the films one on top of the other accordingly, whereupon this is passed through a heated gap and is bonded to form a composite layer plate or film under pressure and heat.

Moreover, a protective layer can be applied to a surface of the film layer, for example a polyethylene film protective layer and preferably temporarily. It is advantageous to laminate the protective layer onto the still warm top surface of the film using known laminating methods directly after the production of the film layer, for example after the co-extrusion of a multi-layered film made of a substrate, if necessary a decorative and a cover layer. This protective layer can be removed at any time during the manufacture or further use of the composite film or rear-injected/rear-pressed moulded part.

The production of moulded parts, in particular vehicle parts such as fenders, door panelling, bumpers, spoilers and side view mirrors, from the composite layer films can be done according to known methods. For example, composite layer films with the three-layer construction of substrate layer, intermediate layer and cover layer, or the two-layer construction of substrate layer and cover layer can be pre-moulded through thermoforming. Positive as well as negative thermoforming methods can be used. Corresponding methods are known to one trained in the art. The composite layer films according to the invention are stretched in the thermoforming process. Since the shine or surface quality of the composite layer films according to the invention does not decrease with stretching at high stretch ratios, for example up to 1:5,

thermoforming methods [present] almost no limitations in practice as to the possible stretching lengths.

By rear-injecting the composite layer films with a fibre-reinforced synthetic material, the moulded parts according to the invention are obtained. Preferably, thermoplastic moulding compounds based on ASA or ABS polymers, SAN polymers, poly(meth)acrylates, polyether sulfones, polyamides, polybutylene terephthalate, polycarbonates, polypropylene (PP) or polyethylene (PE) are used as the synthetic materials, as well as blends of ABS or ASA polymers and polycarbonates or polybutylene terephthalate and blends of polycarbonates and polybutylene terephthalate, wherein if PE and/or PP are used, the substrate layer can be provided with an adhesive layer (0) up front. Especially suitable are amorphous thermoplastics or blends thereof. Preference is given to ABS polymers and blends thereof as the synthetic material for the rear-injection, for example with polycarbonates, polybutylene terephthalate or polyamides.

Especially suitable ABS polymers contain the following components:

- A') 5 to 70, preferably 8 to 65 weight-% of at least one graft copolymer A'), comprising the following based on A'),
  - a1') 10 to 90 weight-% of at least one rubber-elastic graft base with a glass transition temperature of less than 0°C, obtainable through polymerization of, based on a1'),
    - a11') 60 to 100, preferably 70 to 100 weight-% of at least one conjugated diene and/or C<sub>1</sub>- to C<sub>10</sub>-alkyl acrylate, in particular butadiene, isoprene, n-butyl acrylate and/or 2-ethylhexyl acrylate,
    - a12') 0 to 30, preferably 0 to 25 weight-% of at least one other monoethylenically unsaturated monomer, in particular styrene,  $\alpha$ -methyl styrene, n-butyl acrylate, methyl methacrylate or mixtures thereof, in particular with regard to the latter butadiene/styrene and n-butyl acrylate/styrene copolymers, and
    - a13') 0 to 10, preferably 0 to 6 weight-% of at least one cross-linked monomer, preferably divinyl benzene, diallyl maleate, allyl esters of (meth)acrylic acid, dihydrodicyclopentadienyl acrylate, divinyl esters of dicarboxylic acids such as succinic and adipic acid as well as diallyl and divinyl ethers of bi-

functional alcohols such as ethylene glycol or butane-1,4-diol,

- a2') 10 to 60, preferably 15 to 55 weight-% of a graft overlay a2'), comprising the following based on a2'),
  - a21') 50 to 100, preferably 55 to 90 weight-% of at least one vinyl aromatic monomer, preferably styrene and/or  $\alpha$ -methyl styrene,
  - a22') 5 to 35, preferably 10 to 30 weight-% of acrylonitrile and/or methacrylonitrile, preferably acrylonitrile,
  - a23') 0 to 50, preferably 0 to 30 weight-% of at least one other monoethylenically unsaturated monomer, preferably methyl methacrylate and n-butyl acrylate, and
- B') 29 to 90, preferably 34 to 88 weight-% of a hard copolymer comprising, based on B'),
  - b1') 50 to 100, preferably 55 to 90 weight-% of at least one styrene compound, in particular styrene and/or  $\alpha$ -methyl styrene,
  - b2') 0 to 50 weight-% acrylonitrile or methacrylonitrile or mixtures thereof,
  - b3') 0 to 50 weight-% of at least one other monoethylenically unsaturated monomer, for example methyl methacrylate and N-alkyl or N-aryl maleic imides such as N-phenyl maleic imide.

Contained in these ABS polymers can, moreover, be triple block copolymers EO-PO-EO with a middle PO block comprising propylene oxide units and terminal EO blocks comprising ethylene oxide units, for example the commercial product Pluronic® (by BASF).

As stabilizers, the ABS polymers can moreover contain butylated reaction products of p-cresol with dicyclopentadiene, for example the commercial product Wingsty®L (by Goodyear), thiocarboxylic acid esters such as thiodipropionic acid dilauryl ester (such as Cyanox® LTPD; made by American Cyanamid) and alkali or alkaline earth metal salts of a C<sub>6</sub>- to C<sub>20</sub>-carbonsaeure, such as magnesium or potassium stearate.

The production and general and special embodiments of the above mentioned ABS polymers are described in detail in the as yet unpublished German patent application

DE 10026858.7, to which express reference is made here.

ABS polymers derive from the following in another preferred embodiment;

- A") 5 to 80, preferably 10 to 70 weight-% of a graft polymer A") with a bimodal particle size distribution comprising, based on A"),
  - a1") 40 to 90, preferably 45 to 85 weight-% of a rubber-elastic particulate graft base a1'), obtained through polymerization of, based on a1"),
    - a11") 70 to 100, preferably 75 to 100 weight-% of at least one conjugated diene, in particular butadiene and/or isoprene,
    - a12") 0 to 30, preferably 0 to 25 weight-% of at least one other monoethylenically unsaturated monomer, in particular styrene,  $\alpha$ -methyl styrene, n-butyl acrylate, or mixtures thereof,
  - a2") 10 to 60, preferably 15 to 55 weight-% of a graft overlay a2"), comprising the following based on a2"),
    - a21") 65 to 95, preferably 70 to 90 weight-% of at least one vinyl aromatic monomer, preferably styrene,
    - a22") 5 to 35, preferably 10 to 30 weight-% of acrylonitrile,
    - a23") 0 to 30, preferably 0 to 20 weight-% of at least one other monoethylenically unsaturated monomer, preferably methyl methacrylate and n-butyl acrylate, and
- B") 20 to 95, preferably 30 to 90 weight-% of a thermoplastic polymer B") with a viscosity index VZ (determined according to DIN 53726 at 25°C in a 0.5 weight-% solution in dimethyl formamide) of 50 to 120 ml/g, comprising, based on B"),
  - b1") 69 to 81, preferably 70 to 78 weight-% of at least one vinyl aromatic monomer, preferably styrene and/or  $\alpha$ -methyl styrene,
  - b2") 19 to 31, preferably 22 to 30 weight-% acrylonitrile,



- b3") 0 to 30, preferably 0 to 28 weight-% of at least one other monoethylenically unsaturated monomer, for example methyl methacrylate or N-alkyl or N-aryl maleic imide such as N-phenyl maleic imide.

In one embodiment, components B") in the ABS polymers exist in succession, said components differing from one another in their viscosity indices VZ by at least five units (ml/g) and/or in their acrylonitrile contents by five units (weight-%). Moreover, in parts, component B") materials can exist in which the acrylonitrile content is greater than 31 weight-%, in particular up to 37 weight-%, in addition to the moulding compound described above under B"). Finally, in addition to component B") and the other embodiments, copolymers comprising styrene and maleic acid anhydride or maleic imides, styrene, maleic imides and methyl methacrylate or acrylonitrile, or comprising styrene, maleic imides, methyl methacrylate and acrylonitrile can also be added.

In these ABS polymers, the graft polymers A') and A") are preferred to be obtained through emulsion polymerization. The mixing of graft polymers A')/A") with components B') and B") and if necessary other additives is done in a mixing device, wherein an essentially molten, flowing polymer mixture results. It is advantageous to cool the molten, flowing polymer mixture as quickly as possible.

Otherwise, the production and general as well as special embodiments of the ABS polymers identified above are described in detail in German patent application DE-A 19728629, to which express reference is made hereby.

The ABS polymers identified can contain other common aids and fillers. Such materials include lubricants or de-moulding agents, waxes, pigments, dyes, flame retardants, antioxidants, light stabilizers or antistatic agents, for example.

The synthetic material used for rear-injection according to the method of the invention comprises long fibres in an amount of in general 3 to 40 weight-%, preferably 7 to 25 weight-% and in particular from 10 to 20 weight-%. Examples of fibrous fillers are carbon, aramid or glass fibres, cut glass or glass thread rovings. Especially preferred are glass fibres. Moreover, natural fibres such as flax, hemp, jute, sisal, ramie or carnauf can be used as said fibres.

The glass fibres used can be E, A or C glass and are preferred to be provided with a sizing agent and/or an adhesion promoter. Its diameter is in general between 6 and 30  $\mu\text{m}$ . Both continuous fibres (rovings) and cut glass fibres (staples) with a length of 1 to 30 mm, preferably 3 to 20 mm, can be used.

As regards the invention, the definition of a long fibre-reinforced synthetic material is if the fibre length contained in it is larger than or equal to 0.5 mm, preferably 0.7 mm and more preferably 1.0 mm (number-average). Long fibre-reinforced synthetic material therefore exists in particular if in the rear-injected moulded part in general at least 10 weight-%, preferably at least 30 weight-%, and more preferably at least 50 weight-% of all fibres have a length of greater than 1 mm, in particular larger than 1.5 mm. Suitable sizing agents are composed of amino silanes, polyesters or epoxide, polyurethane or phenol resins, or of any arbitrary mixtures of these sizing agents, for example, and are commercially available either directly or are already applied to commercial glass fibres by the glass fibre manufacturer.

Suitable particulate fillers include amorphous silica, magnesium carbonate, powdered quartz, glimmer, mica, bentonite, talc, feldspar or in particular calcium silicate and wollastonite and kaolin, in addition to carbon black.

For the rear-injection of composite layer films with fibre-reinforced synthetic material, plastic and fibre material are added together, melted and mixed in an extruder or an injection moulding machine, either which contains at least one distributive mixing element in the area adjacent to the compression zone, prior to the rear-injection. Preferably, all synthetic material is located behind the compression zone in molten form. In extruders, the compression zone is also called the transition zone (see also Saechtling, *Kunststoff Taschenbuch*, 27<sup>th</sup> Edition, Carl Hanser Verlag, Munich, 1998, page 244 through 247).

Possible distributive mixing elements include rhombic or rod or cam mixing parts, or those with openings in the windings for example. Suitable mixing parts are also described in "*Einfärben mit Kunststoffen*" publisher, VDI Gesellschaft Kunststofftechnik, VDI Verlag, Düsseldorf, 1975, page 261 through 265. Preference is given to a special mixing ring as the mixing element which is located between the housing of the extruder or injection moulding machine (also called the stator) and the scroll (also called the rotor) freely around the scroll, and which is provided with a

series of apertures that extend around the perimeter. This element is called a Twente mixing ring in abbreviated form. The apertures can assume regular or irregular geometric forms, are in general however, circular or oval in shape. They can moreover be arranged in irregular order or in circular tracks along the mixing ring. Moreover, the scroll, i.e. the rotor, can have indentations under the mixing ring that can be aligned with the apertures of the mixing ring or can be displaced relative to them. The indentations can coincide in peripheral shape with the apertures in the mixing ring, but can also deviate from them in size and shape. The indentations usually have the shape of partial sections of a sphere or an ellipsoid, and therefore represent hemispherical or semi-ellipsoidal indentations for example, wherein a continuous transition from rotor surface and indentation to an abrupt, sharp-edged transition is preferred. Especially suitable embodiments of extruders or injection moulding equipment containing a special mixing ring containing apertures are also described in EP 340 873 B1 and in DE 42 36 662 C2, which are expressly incorporated by reference into this disclosure.

Preferably, the production of the film rear-injected plastic moulded parts in a multi-stage process is done by

- a) Producing the film, in particular the composite layer film using adapter or nozzle (co)extrusion of cover, substrate and if necessary intermediate layer, wherein the entire film composite is produced preferably in a single stage process,
- b) if necessary thermoforming the composite layer film in a moulding tool and
- c) rear-injecting the composite layer film with the fibre-reinforced synthetic material, wherein the synthetic material and fibre material are added together, melted and mixed in an extruder or an injection moulding machine, both of which contain at least one distributive mixing element in the area adjacent to the compression zone, prior to the rear-injection.

The plastic moulded parts according to the invention can be used in vehicle areas, in particular exterior vehicle body parts, for example for smaller exterior vehicle body parts such as mirrors or dressings or for large area exterior body parts such as fenders, hoods, covers, doors, bumpers or shock absorbers. Moreover, other possible

applications include internal panelling parts for vehicles, such as door side panels, A, B and C and steering wheel panels, instrument panels and panel elements in the floorboard area of vehicles, as well as applications for internal airplay components, internal boat components, housing for household and electronic appliances, garden furniture, battery cases, window profiles, façade panelling, doors, floor coverings, cell phone housings or seat shells.

The moulded parts according to the invention have a very satisfactory breakage behaviour and very good impact resistance even at low temperatures. This applies in particular when ABS polymers are used as the rear-injected material. No unevenness, in particular no glass nodules, are observed on the film side nor on the back of the film rear-injected moulded part, not even in a climate change test.

Finally, it is possible according to the method according to the invention to obtain a strengthened synthetic material using long fibres by incorporating the fibre material directly into the synthetic material in homogeneous form. In contrast to conventional methods, it is no longer necessary to add the long fibres to the synthetic material via a granulate or polymer pellet containing the long fibres. To the contrary, fibre and synthetic material can be mixed cold prior to feeding to the extruder. Likewise, it is possible to add the fibre material separately to the polymer granulate located in the mixing and melting equipment such as an extruder. The polymer granulate can in the process exist as a melt, partially melted or unmelted.

The surface of the moulded parts according to the invention is not affected by the use of fibre-reinforced products. For example, rear-injected long glass fibre-reinforced products comprised of ABS polymers (average fibre length in the component approximately 0.7 to 2 mm (weight average) have a perfect surface. Even on the non film-coated side, no fibres can be detected.

In mechanical tests such as the head impact test, rear-injected samples that are produced using long fibre-reinforced synthetic material, such as ABS polymer, in particular at low temperatures, exhibit a very good breakage behaviour and very good toughness. Even with an average fibre length of 0.7 mm (weight average), in the synthetic material, very good mechanical properties have been determined, in

particular regarding breakage behaviour and toughness.

The combination of long fibre-reinforced synthetic materials, in particular ABS polymer, as a rear-injection material (thickness preferred to be 2 to 3 mm) with a composite layer film of un-reinforced polymers makes it possible to produce Class A components that can be produced without painting and that exhibit an E-modulus of greater than 3000, preferably greater than 3200 MPa and a thermal longitudinal elongation of less than  $50 \times 10^{-6}$  1/K and a non-splintering breakage pattern at low temperatures. The breakage pattern following the head impact test at  $-30^{\circ}\text{C}$  is even more favourable than when using an un-reinforced thermoplastic.

The invention is further explained with the aid of the following examples.

Examples:

The rear-injected moulded parts were produced with a Krauss Maffei 1500 injection moulding machine. In the variant according to the invention, a standard three-zone scroll with a diameter of 115 mm and a Twente mixing ring made by Maas International (NL-Wierden) was used. In the non-invention related variants a common standard three zone scroll made by Krauss Maffei with a diameter of 105 mm was used. The temperature profile of the injection moulding machines were as follows: 210/250/260/260/260°C,

For the rear-injection, the commercial product Terluran® GP 22 (BASF AG) was used as the ABS synthetic material (I).

The following glass fibres (II) were used:

- i) Crotec® 152A-14C (13 mm cut length, Owens Corning)
- ii) Crotec® 183F-11C (4 mm cut length, Owens Corning).

The rear-injected film (III) is composed of a substrate layer (1) as the support film (900 µm) of a commercial ASA copolymer (Luran® S, BASF AG), and a cover layer (3) (100 µm), likewise made of a commercial polymethyl methacrylate (Lucryl®, BASF AG).

The components of the individual layers (1) and (3) were each separately melted and homogenized in an extruder at 230 to 250°C. The melt streams were laid on top of

one another in a feed block in front of the entrance to the wide slit nozzle and stretched as a layered composite to the width of the nozzle (1.2 m)

The ABS (I) and the glass fibre material (II i) and ii)) (15 weight-%, based on fibre-reinforced ABS polymer) were added to the injection moulding machine cold mixed. Car trunk lids with a size of 400x1200x3.2 mm were produced via an injection moulding tool in which the composite film (III) was positioned.

The rest of the results are summarized in the following Table 1.

Table 1

Example	Glass Fibre (II)	Glass nodules / Surface <sup>b)</sup>	Impact Resistance [kJ/m <sup>2</sup> ]	Tensile Strength [Mpa]	Elongation at Break [%]
1	i)	-/very good	20	52	2.7
2 <sup>a)</sup>	ii)	+/- bad	18	51	2.9
3 <sup>a)</sup>	i)	+/-bad	19	48	2.6
4 <sup>a)</sup>	Ultradur® S 4090 G6	-/very good	18	40	1.1

a) Comparison Example

b) The rear-injected comparison moulded parts according to Example 2 and 3 were produced conventionally without the use of mixed parts. Glass nodules were seen on the side opposite the film, and on the film side glass nodules became clearly apparent in a climate change test at temperatures in the range of -40 to +90°C. Example 1 exhibited no impairment or modification of the perfect surface in the climate change test and no worsening of the mechanical properties.

The comparison moulded part according to Example 4, likewise produced without using mixed parts, in which the glass fibres have an average length of about 0.3 mm in the polymer matrix (weight average), exhibits a much lower elongation at break and tensile strength compared to the components according to the invention. Here, the glass fibres, embedded in a polymer granulate, i.e. as pelletized granulate, were worked into the polymer matrix to be melted.

The climate change test was carried out under the following conditions which are common for automobile components: 3 cycles at 15h each at 90°C, 30 min at 23°C, 8 h at -40°C and 30 min at 23°C.

Impact resistance was determined on sample bodies that were mechanically prepared according to ISO 179/1eU from the trunk lids of size 80 x 10 x 3.2 mm.

The tensile tests were carried out according to ISO 527-2 at 23°C at a pull rate of 5 mm/min.

## Patent Claims

1. A method to produce film rear-injected plastic moulded parts comprising a film and a long fibre-reinforced synthetic material, wherein the film is positioned in a moulding tool and rear-injected with a synthetic material reinforced with a fibre material to form a moulded part, characterized in that prior to the rear-injection, synthetic material and fibre material are added together, melted and mixed in an extruder or an injection moulding machine that contains at least one distributive mixing element in the area adjacent to the compression zone.

2. A method according to claim 1, characterized in that the mixing element comprises a special mixing ring that is located between the housing of the extruder or the injection moulding machine (stator) and the scroll (rotor) freely placed around the scroll and containing a series of apertures that extend around the perimeter, and that the scroll contains indentations beneath the mixing ring.

4. A method according to claim 3, characterized in that the composite layer film comprises:

a) a substrate layer (1) containing ASA polymers, ABS polymers, polycarbonates, polyesters, polyamides, polyether imides, polyether ketones, polyphenylene sulfides, polyphenylene ethers or mixtures thereof,

b) if necessary an intermediate layer (2), containing poly(meth)acrylates, impact-resistant poly(meth)acrylates, poly(meth)acrylamides, poly(meth)acrylonitrile, ASA polymers, ABS polymers, polycarbonates, polyesters, polyamides, polyether sulfones, polysulfones, polyvinyl chloride or mixtures thereof, and



c) a transparent cover layer (3), containing poly(meth)acrylates, impact-resistant poly(meth)acrylates, fluorine (co)polymers, ABS polymers, polycarbonates, polyethylene terephthalate, amorphous polyamide, SAN polymers, polyether sulfones, polysulfones or mixtures thereof.

5. A method according to claims 3 or 4 [sic], characterized in that the substrate layer is constructed essentially of ASA polymers and if necessary polycarbonates.

6. A method according to claims 3 through 5 [sic], characterized in that ASA polymers consist essentially of:

- a) 1 to 99 weight-% of a graft copolymer (component A) comprising
  - a1) 1 to 99 weight-% of a particulate graft base A1 comprised of monomers
    - a11) 80 to 99.99 weight-% of at least one C<sub>1</sub>- to C<sub>8</sub> alkyl ester of acrylic acid as component A11,
    - a12) 0.01 to 20 weight-% of at least one poly-functional cross-linked monomer as component A12.
  - a2) 1 to 99 weight-% of a graft overlay A2 comprising monomers, based on A2,
    - a21) 40 to 100 weight-% styrene units, substituted styrene units or (meth)acrylic acid ester units, or mixtures thereof as component A21 and
    - a22) 0 to 60 weight-% acrylonitrile or methacrylonitrile units as component A22,  
wherein the graft overlay A2 consists of at least one graft shell and wherein the graft copolymer has an average particle size of 50 to 100 nm; and
- b) 1 to 99 weight-% of a copolymer (component B) comprising
  - b1) 40 to 100 weight-% styrene, substituted styrene or (meth)acrylic acid ester units or mixtures thereof as component B1,

b2) 0 to 60 weight-% acrylonitrile or methacrylonitrile units as component B2.

7. A method according to claims 1 through 6 [sic], characterized in that the synthetic material used is an ABS polymer, polybutylene terephthalate or a mixture of polycarbonate and polybutylene terephthalate or a mixture of an ASA polymer and polycarbonate or an ASA polymer and polybutylene terephthalate.

8. A method according to claims 1 through 7 [sic], characterized in that the fibres in the rear-injected plastic moulded part have an average fibre length of greater than or equal to 0.5 mm (number-average).

9. Rear-injected plastic moulded parts, obtained according to one of claims 1 to 8.

10. Use of the plastic moulded parts according to claim 9 as internal or external body parts, internal airplane components, internal boat components, housings for household and electronic appliances, garden furniture, battery cases, window profiles, façade panelling, doors, floor coverings, cell phone housing or seat shells.

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(54) **Title:** METHOD FOR THE PRODUCTION OF FILM REAR-INJECTED PLASTIC MOULDED PARTS  
AND FILM REAR-INJECTED PLASTIC MOULDED PARTS

(57) Method for the production of film rear-injected plastic moulded parts comprising a film and a long fiber-reinforced synthetic material, wherein the film is positioned in a moulding tool and rear-injected with a synthetic material reinforced with a fiber material to form a moulded part, wherein the synthetic material and fibre material are added together, melted, and mixed prior to the rear injection in an extruder or an injection moulding machine which have at least one distributive mixing element in the area adjacent to the compression zone, and plastic moulded parts obtained according to this method.



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